LETTERS TO THE EDITORS

THE OXIDATION-REDUCTION POTENTIAL OF COENZYME I

Sirs:

The oxidation-reduction potential of cozymase (diphosphopyridine nucleotide) was calculated from the free energies of formation of aqueous *d*-alanine and *d*-glutamic acid based on thermal data, and the equilibria measured by Wurmser and Filitti-Wurmser[1] for pyruvate + $2H^+$ + $2(e) \rightleftharpoons$ alanine + H_2O, by Cohen[2] for α-ketoglutarate + alanine $\rightleftharpoons$ *d*-glutamate and pyruvate, and by von Euler *et al.*[3] for the reaction α-ketoglutarate + NH_4^+ + reduced cozymase $\rightleftharpoons$ glutamate + oxidized cozymase. The value for the potential so calculated is at 30° $E'_0 = -0.072 - 0.03$ pH $\pm$ 0.0008 volt.

Its temperature coefficient is $\Delta\tilde{E}/\Delta T = -0.00043$, calculated from the data given by von Euler, Adler, Günther, and Hellström[4] and by Barron and Hastings.[5]

As a check on the accuracy of this calculated value of $\tilde{E}$ it was used to calculate $-\Delta\tilde{F}$ for the reaction acetaldehyde (aqueous) + $2H^+$ + $2(e) \rightarrow$ ethyl alcohol (aqueous) from the equilibrium constant for acetaldehyde + reduced cozymase $\rightleftharpoons$ ethyl alcohol + oxidized cozymase determined by Negelein and Wulff.[6] This constant (corrected for temperature) and the above value of $\tilde{E}$ give $-\Delta\tilde{F}$ for acetaldehyde $\rightarrow$ alcohol at 25° as 11,620 calories. $-\Delta\tilde{F}$ calculated from the best thermal and ancillary data is 11,730 calories.

[1] Wurmser, R., and Filitti-Wurmser, S., *Compt. rend. Soc. biol.*, **128**, 133 (1938).

[2] Cohen, P., *Biochem. J.*, **33**, 1478 (1939).

[3] von Euler, H., Adler, E., Günther, G., and Das, N. B., *Z. physiol. Chem.*, **254**, 61 (1938).

[4] von Euler, H., Adler, E., Günther, G., and Hellström, H., *Z. physiol. Chem.*, **245**, 217 (1937).

[5] Barron, E. S. G., and Hastings, A. B., *J. Biol. Chem.*, **107**, 567 (1934).

[6] Negelein, E., and Wulff, H.-J., *Biochem. Z.*, **293**, 351 (1937).

The data of Green and Dewan[7] on the reaction acetoacetate + reduced cozymase → β-hydroxybutyric acid + oxidized cozymase, and the E'_0 values of Hoff-Jørgensen[8] for the acetoacetate → β-hydroxybutyrate give E'_0 for the cozymase (corrected to 30°) at pH 7.0 −0.289, −0.275, and −0.274. The calculated value is −0.282.

Ball and Ramsdell[9] recently reported for cozymase a tentative value of E'_0 at pH 7.2 and 25° of −0.26 volt. The difference between this and the above calculated value (more than 0.020 volt) may possibly reside in Ball and Ramsdell's having used a flavoprotein as enzyme. With this protein the ratio of the association constants for the reduced and oxidized cozymase may be very different from those with the proteins of the glutamic acid, ethyl alcohol, and β-hydroxybutyric acid dehydrogenases.

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[8] Hoff-Jørgensen, E., *Skand. Arch. Physiol.*, **80**, 176 (1938).
[9] Ball, E. G., and Ramsdell, P. A., *J. Biol. Chem.*, **131**, 767 (1939).